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Technical Report
to the
Office of Naval Research

on

The Interaction of Sulfate Ions with Iron Surfaces

by

Norman Hackerman and Sarah J. Stephens

1 July 1953

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The Interaction of Sulfate Ions with Iron Surfaces

by

Norman Hackerman and Sarah J. Stephens

Summary

Data were obtained showing the adsorption of sulfate ions from aqueous solutions onto iron surfaces under various conditions. The amount of sulfate adsorbed was determined using radioactive tracer techniques. An air-free system was used.

An adsorption isotherm showing the adsorption of sulfate ions onto iron at room temperature and pH 7 indicated that at maximum adsorption 0.35 of the surface was covered by sulfate ions.

Isotherms were obtained using mixed solutions of sulfate and chromate, and sulfate and chloride. In each case the pick-up of sulfate was followed. It was found that the chromate ion competes strongly with the sulfate ion when present in the solution in equal or greater concentration. The presence of chloride ion, on the other hand, increases the amount of sulfate ion adsorbed except at very high concentrations of chloride ion, when it completely prevents adsorption of sulfate.

The effect of pH on the adsorption of sulfate ions was determined. While hydroxyl ions apparently adsorbed on the surface at the lower pH values used (pH 7 to 10) there was no decrease in the amount of sulfate adsorbed until a pH between 10 and 11 was reached, when the adsorption of sulfate began to drop sharply. At pH 12 there was almost no pick-up of sulfate ions.

Preparation of the surface had a very noticeable effect on the amount of adsorption. Coupons which had been abraded and treated with chromate solution adsorbed much less sulfate than coupons which had been abraded in the same way but not treated with chromate. Highly polished coupons acquired much greater activity than coupons which were less highly polished, presumably because of the greater amount of oxide present on the surface.

A study of the amount of adsorption as a function of time showed that the activity picked up increased for about two hours, then remained fairly constant for a while, and finally decreased slowly until it reached a constant value at about fourteen hours. The activity on the surface when this constant value was reached was very firmly held and could not be removed by washing at temperature. The activity on coupons exposed for shorter periods of time could be removed by repeated washings, except for a certain fraction which seemed to be firmly held.

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All isotherms were obtained with coupons which were exposed to the solutions for sixteen hours. The sulfate picked up on the surface of the iron under these conditions was chemisorbed, and could not be removed other than by destroying the surface.

The sulfate is believed to adsorb on the oxide covering the surface. This is substantiated by data showing an increase in the amount of activity picked up with increase in the amount of oxide on the surface. In the air-free system used no reaction takes place between the iron and the substances in solution, so that all activity picked up represents true adsorption.

Introduction

Ionic adsorption on metals has been detected indirectly by its effect on the electrocapillary curve of mercury (1). Paneth (2) determined the specific surface areas of lead salts by adsorbing thorium B on them from solution. Thorium B was also used by von Hevesy (3), (4) to show that exchange occurs between a metal and its ions in solution. In this case 1,000 atomic layers were said to be involved.

Broader use of radio tracers in following directly the interaction of ions in solutions, and metals exposed to these solutions waited upon the present greater availability of radioisotopes. Rollin (5) and Coffin and Tingley (6) showed that radioactive silver ions in solution exchange with metallic silver, and that gold and platinum also acquire activity when exposed to the silver solution. There was no proof that the latter were exchange phenomena rather than simple adsorption, but exchange with non-common ions is also possible.

Hensley, Long, and Willard (7) showed that sodium ions are adsorbed from aqueous solutions by soft glass, and also by aluminum, steel, silver, and platinum. Simnad and Ruder (8) studied the exchange between radioactive cobalt in solution and a number of metals, both in the presence and absence of oxygen. They found that in the absence of oxygen, activity of the solid on the surface increased with time of exposure to an asymptotic value, but in the presence of oxygen it reached a maximum quickly and then decreased with time. In the presence of oxygen the amount of activity picked up was increased greatly. Ground iron surfaces, in the absence of oxygen, picked up far less activity than etched surfaces. The authors concluded that the amount of radioactivity acquired was the result of cations being deposited on the surface by local cell action. Where the oxide film on the metal was not protective, as in the case of iron, the presence of oxygen increased the amount of activity picked up by acting as a depolarizer.

The adsorption of radioactive cobalt onto hydrous ferric oxide in the presence of ammonia and ammonium chloride was studied by Kurbatov, Wood, and Kurbatov (9), and adsorption isotherms were obtained using the procedure of coprecipitation. The effects of pH, concentration, and amount of adsorbent on the quantity of cobalt ions adsorbed were determined.

Although the above mentioned work does much to elucidate the behavior of metals in solutions, it deals solely with the relationship between cations in solution and the metal, or metal oxide. Attempts to study the adsorption of anions from solution were made by Marshall (10) using Cl^{36} as tracer in NaCl solutions with chromium sorbent. The results were equivocal because of low activity of the tracer and contamination with S^{35} . Further work along this line was undertaken here on the adsorption of chromate and sulfate ions on chromium (11) and steel (12) surfaces. The major portion

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of the work involved study of the chromium metal-chromate ion system under various conditions, and showed that chromate ions were firmly acquired by the surface.

There is here the possibility of chemical reaction, so that it is difficult to tell if it is truly adsorption that is taking place. The studies using steel showed that in chromate solutions of high enough concentration to cause complete passivation, a definite amount of activity was picked up, and that this activity was uniformly distributed over the surface. At lower concentrations corrosion took place and the activity picked up increased; a certain amount being distributed over the surface as before, but the greater part being associated with the cathodic parts of the surface, as shown by autoradiographs.

The present work was done with iron using the sulfate ion as adsorbate, with $S^{35}O_4^{=}$ as tracer. Since iron corrodes rapidly in salt solutions in the presence of air, an air-free system was used.

The adsorption of sulfate ions on metal surfaces is of interest intrinsically because it gives an insight into the kinetics of metal-solution reactions. Also the sulfate ion, if it adsorbs on this surface, should not react, since there is no evidence to show that the local cells on the metal can provide sufficiently high anodic or cathodic potentials to cause sulfate ions to undergo electrochemical reaction. The chromate ion, on the other hand, which can render the surface passive, may react with the dissolving iron, being incorporated into the surface film as trivalent oxide. It may, besides reacting, also adsorb on the surface. The chloride ion destroys passivity, in a manner not yet clear. One explanation suggests that it can penetrate the film readily, but this is not based on firm evidence. Another unproved possibility depends on the fact that it complexes metal ions so effectively. The chloride ion apparently adsorbs on metal surfaces, as shown by Marshall (10).

Sulfate as $S^{35}O_4^{=}$ is available in carrier-free solutions from the United States Atomic Energy Commission. It is of sufficiently high activity so that large counts can be obtained using short counting times, and the counts are high compared to background. Sulfur-35 has a half-life of 87.1 days, so that samples of active sulfate obtained from Oak Ridge can be used a fairly long time. In this work active solutions were never used for more than three half-lives.

The study includes the effect of other anions on the sulfate sorption as well as the influence of surface pretreatment.

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Experimental

Preparation of Active Sulfate Solution. The active sulfate ($S^{35}O_4^{=}$) of 87.1 day half-life was obtained in the form of carrier-free sulfate in dilute (usually around 0.1 N) hydrochloric acid, the total activity being 10 millicuries in 0.2 ml. The solution was diluted to about 2 ml. for ease in handling and to provide a greater volume of active solution, then prepared for use as described by Powers (13). In order to remove chloride ions, the solution was electrolyzed between platinum electrodes until oxygen evolution started, then a silver electrode was substituted for the platinum anode, and the electrolysis continued at a very low current density. In this way silver chloride did not precipitate in the solution but formed on the anode. The final chloride concentration was less than 1×10^{-5} M.

Preparation of Active Chromate Solution. The active chromate ($Cr^{51}O_4^{=}$) solution was prepared by dissolving active chromium metal electrolytically*. This yielded a solution of H_2CrO_4 containing only chromate ions and the ions from water.

Preparation of Active Chloride Solution. The active chloride solution (containing Cl^{36}) was used as it came from Oak Ridge, simply by diluting to the desired concentration and adjusting the pH. The solution contained so much chloride as carrier that when diluted to the proper concentration the activity proved too low to be useful.

Preparation of Iron Coupons. Coupons were cut from sheets of Armco iron 1.6 mm. thick. These coupons were round, 1.9 cm. in diameter. The analysis of the iron, supplied by Armco Steel Corporation, showed the following: C, .010; Mn, .010; P, .005; S, .012; Si, .002; Cu, .040.

Various methods of preparing the iron surfaces were tried and are described in connection with the individual experiments, but the method of preparation of the coupons used in the major portion of the work was as follows: they were washed several times in benzene to remove the bulk of the grease and dirt, then they were abraded with #2 emery paper, wiped with a clean cloth, washed twice in hot benzene, and stored in a desiccator until used. Coupons were always prepared immediately before use, but because of the time involved in setting up the apparatus and removing oxygen from the system, several hours elapsed between the time the coupons were polished and the time they were used. It was found that this lapse of time had no effect. Starting with the polishing operation the coupons were handled only with clean cotton gloves or with tongs which had been carefully cleaned. Coupons prepared in this way were always found to be completely wettable by water.

* This solution was prepared by Sherman Kottle of this Laboratory.

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Preparation of Solutions. Solutions were prepared from Baker's Analyzed Chemicals and double distilled water. A small amount of the active solution was then added; a representative example would be the addition of fifteen microliters of active solution to 50 ml. of 1×10^{-4} M sodium sulfate solution.

Apparatus. In order to work in a system as completely air-free as possible, the adsorption runs were carried out in an 18x18x12" dry box made of lucite. All entrance and exit ports were made by plastic-to-plastic seals. The bottom of the box was a glass plate sealed to the lucite carefully with paraffin. All necessary items, such as tongs, solutions, etc., were placed in the box before each experiment. Tests showed that it could maintain a slight excess pressure (of nitrogen) for a long enough time to serve the purpose of the experiment.

The system was flushed thoroughly with tank nitrogen which first passed through a clean-up train of acidified vanadyl sulfate (14), sodium hydroxide, and water. The gas also flowed continuously during an experiment, and left the system via a water bubbler to prevent air from backing in. The same stream was used to displace dissolved air from the solutions by bubbling it through them in series. There was never any visible carry-over as determined by counting aliquots of the active solutions before and after passing the gas through.

The gas was bubbled through the series of solutions for 15 minutes, the coupons placed in the solutions, and nitrogen bubbled for 15 minutes more. Each solution was then closed off separately. In the solutions, the coupons were supported by short lengths of glass tubing so that the entire coupon was exposed.

After the coupons had been exposed for the necessary period of time, they were removed with tongs, and washed by dipping 20 times in each of three beakers containing about 75 ml. of distilled water each. They were then dried with filter paper, removed from the box, and counted. All runs were made at $28^{\circ} \pm 3^{\circ}$ C.

Analysis for Iron in the Solutions. In order to determine if any iron had dissolved in the solutions, they were acidified with hydrochloric acid and analyzed for iron by the colorimetric method described by Shome (15), using isonitrosodimethyldihydroresorcinol. This method detects iron in solution at a concentration as low as one part in fifty million.

Counting. A standard, thin mica window tube was used. The voltage plateau was determined and the tube was operated in the central region of the plateau at 1300 volts. The coupons were all counted in the same manner, and on the same holder at the same distance from the tube. The background count was determined accurately several times during the time experimental work was being done, and ranged from 24 to 26 counts/minute. The background was always determined roughly (i. e. by counting

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for a short period of time) each time a series of counts was being made in order to find if the coupon holder or the inside of the counting chamber was contaminated with active material. A count of at least 10,000 was always taken, except in some of the earlier work when solutions of very low activity were being used, and only qualitative results were needed. A count of 10,000 gives a standard deviation of one percent. Coincidence corrections were made on the counting data when necessary.

Surface Area Measurement. The true surface area of coupons prepared as described above was determined* by adsorption of krypton at liquid air temperatures as described by Joncich (16). The coupons were found to have a roughness factor of three, or a true surface area three times as great as the apparent area. **

Calculations

Corrections for decay were made from the equation, $A = A_0 e^{-\lambda t}$, where A and A_0 are activities at times t and t_0 respectively, and $\lambda = \ln 2/t_{1/2} = 0.00796 \text{ days}^{-1}$.

The number of ions/count for each active solution was determined by evaporating an aliquot on a glass slide and counting the residue. The value was generally between 2×10^{11} and 5×10^{11} ions/count.

Surface coverage calculations were based on the sulfate ion as a tetrahedron with the sulfur atom at the center and the oxygen atoms at the corners. The S-O distance is 1.32 Å, the O-O distance is 2.43 Å (17), and the ionic radius of oxygen is 1.40 Å (18). The area per sulfate ion is 23.3 Å^2 and the number of these ions in a closed packed monolayer is $4.3 \times 10^{14}/\text{cm}^2$.

* The surface area measurements were made by Nicos Komodromos of this Laboratory.

** It is believed that the roughness factor of 20 used by Powers (12) for steel surfaces prepared in the same manner is not correct. This value was obtained using the electrode polarization capacity method described by him. From attempts made during the course of the present work to measure the roughness factor of iron by this method, it was concluded that while consistent results could be obtained with active metals, the values were always extremely high compared with values obtained by gas adsorption methods. Since the latter are known to give values good to at least 20 percent, the method Powers used must be considered inaccurate at present.

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Results

Preliminary Experiments. Preliminary experiments using SAE 1020 steel coupons showed that unless oxygen was rigidly excluded from the system the results would be erratic; as a matter of fact, the amount of activity picked up depended on the amount of corrosion product formed while the coupon was in the solution. Coupons oxidized by polishing with #4/0 emery until a visible (blue) oxide film was formed adsorbed greater amounts than less highly polished coupons.

Early in the course of the experiments it was decided to use iron of high purity, in order to minimize in so far as possible variations in the sorbing surface.

The first isotherms were run over a wide range of concentrations in order to establish a suitable range for further work, and to establish the experimental method. The general method was to expose a series of coupons, prepared in a particular manner, to air-free solutions of sodium sulfate, containing $S^{35}O_4^{=}$, for a short period of time.

The concentration range was from 0.01 to 1.0 MM, and 10 or 20 ml of solution were used for each exposure. The exposure time was of the order of five minutes; the coupons were then removed with tongs and washed with deaerated water for one minute on each side by means of a wash bottle previously placed in the box. They were then washed with acetone, followed by benzene, and finally dried with filter paper. They were then taken from the box and counted.

In order to see if the sulfate ion was firmly adsorbed, the coupons were washed again for the same length of time as before and counted. Following this they were scrubbed with wet filter paper and counted, for it was thought that any corrosion product which might be present would be removed by scrubbing but not by simple washing. The data are given in Table 1 and plotted in Figure 1 in terms of counts per minute corrected for decay.

TABLE 1

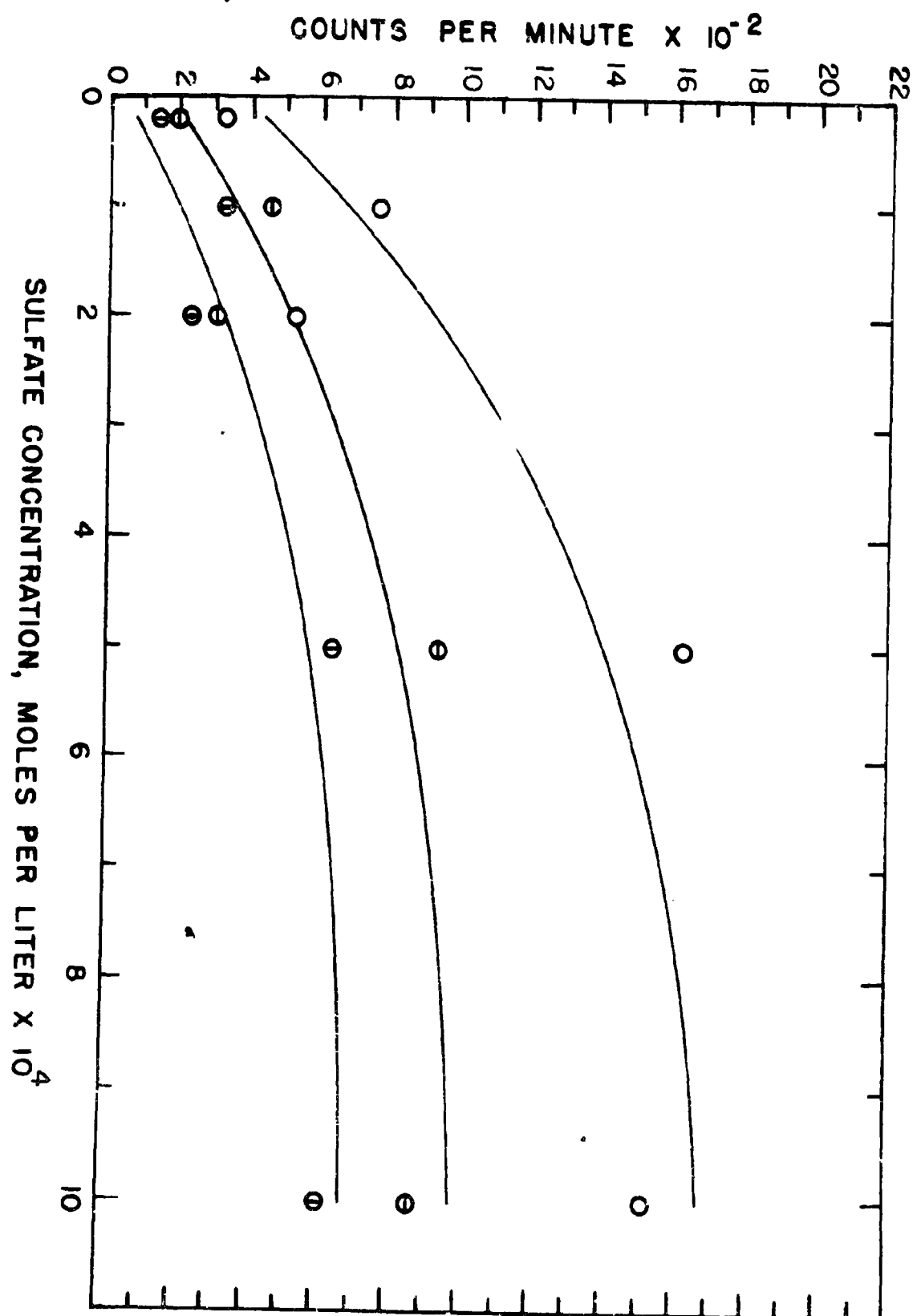
Conc. Na_2SO_4 moles/l.	Count after First Washing	Count after Second Washing	Percent Remaining	Count after Scrubbing	Percent of first Washing Remaining
1.0×10^{-5}	326	200	61	141	43
5.0×10^{-5}	760	454	60	331	44
1.0×10^{-4}	532	310	58	238	45
5.0×10^{-4}	1,620	834	52	637	39
1.0×10^{-3}	1,520	863	57	610	40

Figure 1

**Adsorption of Sulfate Ion on Iron Etched in Hydrochloric
Acid, Showing the Effect of Repeated washing of the Coupon**

Room Temperature pH 7

- First Washing**
- ⊖ Second Washing**
- ⊗ Scrubbing**



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With the solutions in this run, a count of 1600 corresponds to approximately one monolayer. This is the activity of the coupon exposed to the 5×10^{-4} M solution, after the first washing. This is reduced by washing to 0.4 monolayers, and can be reduced still further. Later experiments on rate of adsorption show that in this case coupons were exposed for too short a time to acquire maximum activity and that adsorption under these conditions is not firm. The data, however, did indicate the concentration range in which to work. The solutions were tested for iron, using isonitrosodimethyldihydroresorcinol, and none was detected. Iron was detected on the filter paper used to scrub the coupons, however, indicating that some corrosion had taken place, and that therefore the solutions were not oxygen-free.

A second run was made under the same conditions, except for longer flushing by nitrogen. In this case the activity picked up was much lower, the count after the first washing being about the same as the count found after three washings in the previous run. This activity was more firmly held, however, and a smaller proportion was removed by further washings than in the previous run. This was an indication that, in the first run, oxygen was present in the solutions, and that the activity measured was held in the corrosion product rather than being adsorbed on the surface, and was removed when the corrosion product was removed by washing.

A number of isotherms were obtained using etched coupons, exposing them to the solutions for short periods of time, and varying conditions in an attempt to find those under which consistent, reproducible data could be obtained. Data were more reproducible at low concentrations, and adsorption was firmer. This can be seen from Table 2, in which two separate runs are shown.

Comparison of the two runs shows fairly good agreement at lower concentrations, but wide divergence at higher concentrations, and also shows that the third washing causes little change except for the two highest concentrations at 1×10^{-4} M approximately 0.5 monolayers remain on the surface after three washings.

These isotherms were repeated, except that enough NaCl was added to each solution to make them 1×10^{-3} M with respect to the chloride ion. These data are shown in Table 3.

Comparison of these values with the values when sulfate was used alone shows a significant decrease with addition of chloride in the amount of activity picked up in the lower concentrations, but less effect at the higher concentrations where the chloride to sulfate ratio is not so large. Comparison of individual values such as these can only be qualitative, because of variation in the individual coupons, but is useful when variations are consistent and are large enough to be significant.

A similar run was made in which the same concentrations of sulfate were used, but NaCl was added to all solutions in such quantity that the chloride concentration was 1 M. This reduced the pickup to 5-10 percent of the values obtained with chloride-free solutions, the greatest reduction in activity picked up being in the more dilute solutions.

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TABLE 2

Conc. Na ₂ SO ₄ moles/l.	Count after 1st washing		Count after 2nd washing		Percent Remaining		Count after 3rd washing		Percent Remaining (of 1st washing)	
	Run	2	Run	1	Run	1	Run	1	Run	2
	1	2	1	2	1	2	1	2	1	2
1.2 x 10 ⁻⁵	196	220	148	187	75	85	149	175	75	80
2.5 x 10 ⁻⁵	322	365	288	253	50	69	286	246	89	67
5.2 x 10 ⁻⁵	478	392	413	329	86	84	390	302	82	77
1.0 x 10 ⁻⁴	355	480	335	396	94	83	302	386	85	81
2.0 x 10 ⁻⁴	349	623	286	507	82	81	238	---	68	--
4.0 x 10 ⁻⁴	310	799	267	592	86	74	134	312	43	39

TABLE 3

<u>Concentration</u> <u>Na₂SO₄, moles/l.</u>	<u>Count after</u> <u>3rd washing (c/in)</u>
1.2 x 10 ⁻⁵	65
2.5 x 10 ⁻⁵	196
5.2 x 10 ⁻⁵	106
1.0 x 10 ⁻⁴	189
2.0 x 10 ⁻⁴	272
4.0 x 10 ⁻⁴	227

Effect of Preparation of Surface. After this preliminary work showed that the methods employed could, with proper precautions, give accurate and reproducible results, further work on the preparation of the iron surfaces was undertaken. The work cited above was done with coupons etched with hydrochloric acid, since it was found that coupons so etched were consistently wetted by water, and that fairly reproducible results could be obtained. Coupons prepared by abrading, particularly those polished with finer grades of emery, were often found to be non-wettable by water. It was necessary to study the effect of other methods of preparation of the metal surface, and if possible, to find a method which would not expose the surface to any substances which might adsorb on the surface, such as chloride ions. It was also realized that the short periods during which the coupons were exposed to the solutions were not sufficient for maximum adsorption to take place.

The experimental procedure was the following: the amount of activity picked up by coupons exposed to the solutions for different periods of time was determined, the concentrations of the solutions all being the same, 1×10^{-4} M in Na₂SO₄. Four different kinds of surfaces were prepared, and two separate runs were made with each kind of surface. All coupons received the same preliminary treatment, being abraded with #2 emery, then washed with hot benzene. The four different kinds of surfaces were then prepared as follows: (i) Used without further treatment. (ii) Immersed in 6 N HCl for one minute, then washed in distilled water, acetone, and hot benzene, as before. (iii) Immersed in concentrated HNO₃, washed with distilled water, then with acetone and hot benzene. (iv) Immersed in 1% K₂CrO₄, washed with distilled water, acetone, and hot benzene. The technique employed in making each run was the same as before, except that the coupons were exposed

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to the solutions for 2, 10, and 30 minutes. The data for the two sets of coupons are shown in Table 4. These data are not corrected for time, since they are used only to compare the different surfaces. All counting data were taken over a short time interval. Each value shown in the third column was made with a different coupon, which was then washed again and counted to give the corresponding value in the last column.

Although these data are erratic, they are useful for comparison. The activity of the solutions used at this time was low, so that the count was often not much greater than background. From the continuing increase in activity with time, it is obvious that after 30 minutes adsorption is not complete. In comparing counting data obtained using coupons prepared in different ways, it is assumed that the surface areas of all the coupons are the same. This may not be true, but the variation in surface area would not be great enough to account for the differences observed. There may be appreciable variation between individual coupons prepared in the same way, and so only an average of data from a number of coupons can give reliable results. It is hardly likely, however, that values differing from one another by 100% or more would result from variations in surface area.

It is more likely that the variation is due to the presence of different amounts of oxygen. This would account for the wide variations of the values for coupons immersed for 30 minutes, since more oxygen would diffuse into the solutions during the longer period of time, causing more extensive corrosion. The corrosion product adsorbs anions also and therefore holds activity; this should be removed by continued washing however.

This is the best explanation, since all the coupons except those treated with chromate lose a large amount of their activity on washing. The latter lose a much smaller percentage, probably because they become passive and do not corrode in the presence of oxygen. Prolonged exposure to a solution which did not contain chromate results in corrosion. Coupons treated with concentrated nitric acid were passive, too. However, it was found that the passivity induced in this manner was destroyed so easily that they were almost certainly active again by the time they were put into the solutions. The only difference between these and other active coupons was that their surface was contaminated by whatever material had been adsorbed during their treatment.

Another run was made, with coupons which had no treatment other than being abraded and washed or which had been treated with 1% $\text{Na}_2\text{Cr}_2\text{O}_7$. A sulfate solution of greater activity was used. The data are given in Table 5. The values are the averages of two runs.

The counts per minute at 2 hours correspond (in order) to 0.6, 0.4, 0.4, and 0.3 monolayers.

TABLE 4

Surface	Time of Immersion (minutes)	Counts/Minute 1st Washing	Counts/Minute 2nd Washing
Abraded	2	16	5
		0	0
	10	121	40
		37	5
Etched (HCl)	2	31	16
		39	29
	10	70	52
		72	57
	30	66	44
		141	96
Treated with K_2CrO_4	2	4	1
		1	1
	10	17	12
		13	11
	30	82	34
		30	26
Treated with HNO_3	2	26	24
		16	12
	10	40	43
		28	21
	30	142	162
		112	76

This preliminary work showed that equilibrium had not been obtained during exposure times up to 4 hours, and that further studies along these lines would have to be made. It was also seen that the system was not oxygen-free, and that to eliminate the type of erratic results shown in Table 4, a completely oxygen-free system would be necessary. The oxygen removal system described earlier was started at this point and used for the rest of the work.

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TABLE 5

<u>Time of Immersion</u>	<u>Abraded Coupons</u>		<u>Dichromate Treated</u>	
	<u>c/m, 1st Washing</u>	<u>c/m, 2nd Washing</u>	<u>c/m, 1st Washing</u>	<u>c/m, 2nd Washing</u>
5 min.	459	400	208	110
15 "	1,310	902	635	432
30 "	2,095	1,378	1,360	841
1 hr.	4,840	3,290	2,880	1,862
2 "	6,570	4,370	4,730	3,395
4 "	7,780	5,720		

Study of Activity Picked Up as a Function of the Time of Immersion. The first runs made were in 1.0×10^{-4} M and 1.0×10^{-6} M Na_2SO_4 and extended over a period of 14 hours. The solutions were adjusted to pH 7. The coupons were abraded with #2 emery and washed with hot benzene. These data are shown in Table 5a, and plotted in Figure 2.

TABLE 5a

<u>Time of Immersion</u>	<u>c/m (1.0×10^{-4} M) 1st Washing</u>	<u>c/m (1.0×10^{-6} M) 1st Washing</u>
0.5	2028	---
1	2334	---
2	2558	119
4	----	86
5	2127	---
8	1831	74
11	1276	--
12	1246	--
14	1392	--
16	----	64

Figure 2

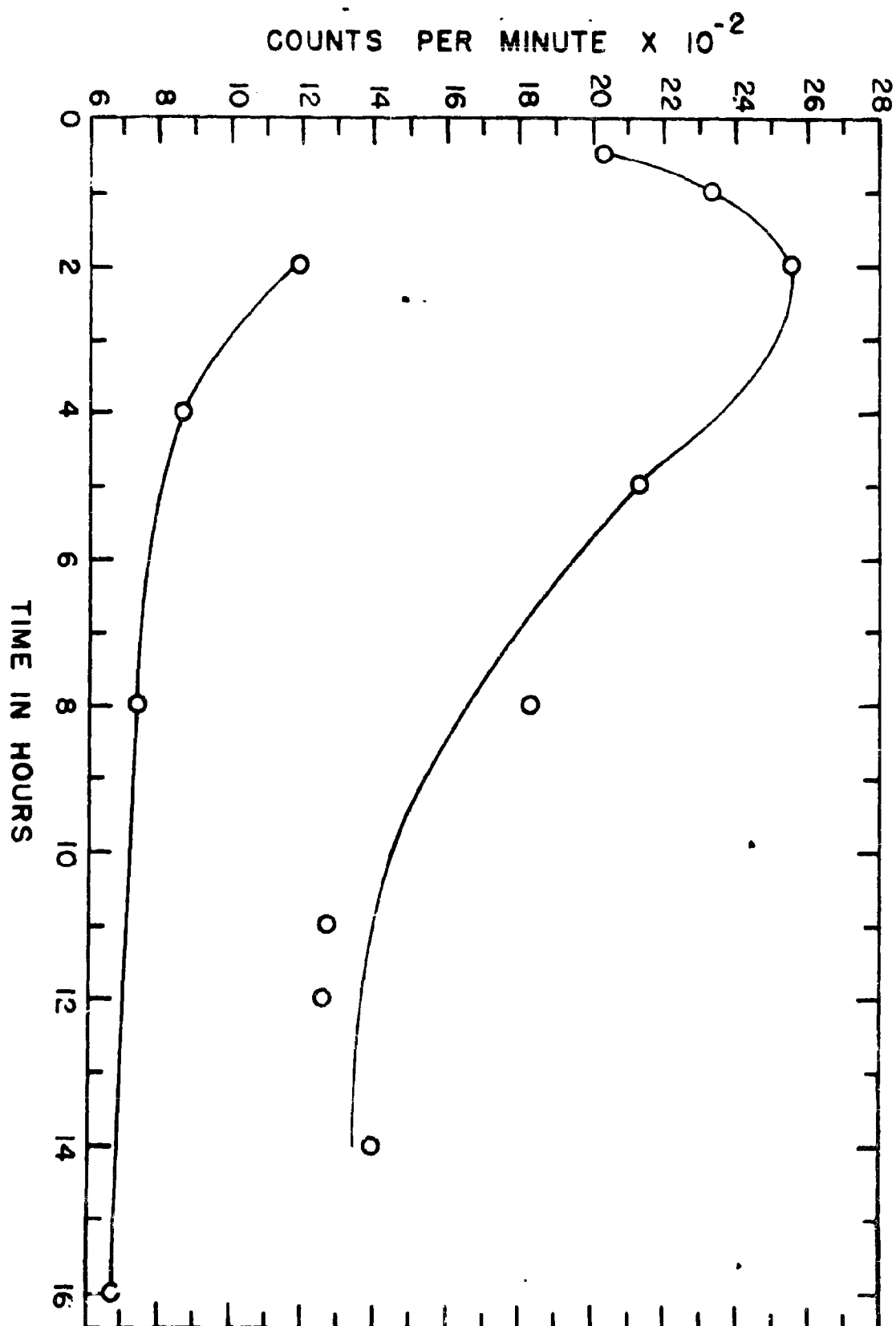
**Adsorption of Sulfate Ion on Iron as a
Function of Time**

Room Temperature, pH 7

Upper Curve-- 1.0×10^{-4} M Na_2SO_4 Solution

Lower Curve-- 1.0×10^{-6} M Na_2SO_4 Solution

(Counts plotted are ten times actual values.)



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The count of 2558 corresponds to 0.4 of a monolayer, and a count of 1250 corresponds to 0.2 of a monolayer. These data are the average of counts on four separate coupons.

The values found for short periods of exposure were much more erratic than those for which the coupons had been exposed for 12 hours or more. The form of the curve is not reproducible, though in all cases it was found that there was an increase in the amount of activity picked up with length of exposure, then a decrease, until a constant value was reached. This is referred to again in the discussion.

Another rate study was made using 1.0×10^{-4} M solutions. The procedure was the same as before, except that after being counted the coupons were washed again for a period of three minutes and counted again. This is a longer period of washing than used in the total of the three washings used previously, and, together with the first washing in the box, should be sufficient to remove sulfate not firmly adsorbed. The data for this run are shown in Table 6, and are directly comparable to those shown in Table 5a, having been corrected to the same t_0 .

TABLE 6

<u>Time of Immersion</u>	<u>c/m (1st Washing)</u>	<u>c/m (2nd Washing)</u>	<u>% Activity Remaining on Coupon</u>
1	1142	645	57
2	1439	1087	75
4	1827	----	--
8	1844	----	--
12	828	706	85
16	552	496	90

The amount of activity is generally lower than that found in the previous run, and the maximum pick-up occurs at an immersion time of eight hours, instead of at two hours as before. It is followed by a much sharper decrease in the amount of activity picked up with time. This is probably not significant, since it was always found that individual coupons gave widely varying results, and it was only when enough runs had been made so that the values from at least four coupons could be averaged that consistent results were obtained.

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In this particular run, only one set of coupons was used, since the purpose primarily was to find if the sulfate adsorbed by coupons exposed to the solution for long periods of time was more firmly adsorbed than that adsorbed over a short period of time. From the previous work, it was seen that often more than 50% of the activity could be removed simply by washing with water. From the results of this run, however, it is seen that more of the sulfate adsorbed over a long period of time is held firmly. This work was followed by a number of experiments on individual coupons, to find how much washing was necessary to remove all sulfate except that firmly held. The method of washing described first was finally adopted and used in all further work.

Sulfate which was adsorbed firmly on the surface could not be removed by washing or scrubbing, but could be removed by etching with HCl or by polishing with emery. In either case, the surface was completely destroyed and removed, and a new surface exposed.

Isotherm Comparing Different Surface Preparations. With this background, a new set of isotherms was run, with particular precautions taken to have the system as oxygen-free as possible. Again, a wide range of concentrations were used, and two simultaneous runs were made, one using coupons polished with #2 emery, the other with #4/0 emery. The coupons were polished, washed in hot benzene, and allowed to stand in a desiccator several hours until used.

The coupons were allowed to remain in the solutions for 17 hours. The results of this run are given in Table 7. The counts are the average of the counts of the front and back of each coupon. These, and all subsequent data, are corrected to the same t_0 , so that all counts are comparable.

TABLE 7

Concentration Na_2SO_4 Moles/l.	c/m (1) Abraded #2 Emery	c/m (2) Abraded #4/0 Emery	Ratio: 2/1
1.0×10^{-6}	53	294	5.6
5.0×10^{-6}	191	697	3.7
1.0×10^{-5}	200	770	3.8
5.0×10^{-5}	849	5,089	6.0
1.0×10^{-4}	652	4,258	6.5
5.0×10^{-4}	843	5,851	7.0
		Average:	5.4

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The amount of activity picked up reached a maximum at a concentration of 5×10^{-5} M. The much greater amount of activity found on the more highly polished coupons is interesting, particularly the values for the last three concentrations, which are fairly constant.

With the known variables studied as described, a firm procedure for reliable results was decided upon and used for all experiments described hereafter.

Adsorption Isotherm, Sulfate on Iron. An isotherm was obtained, using sodium sulfate solutions at pH 7. The data shown in Table 8 and plotted in Figure 3 are the averages from eight different coupons.

TABLE 8

Concentration <u>Na₂SO₄, Moles/l.</u>	<u>c/m</u>
0.2×10^{-4}	189
0.4×10^{-4}	216
0.6×10^{-4}	284
0.8×10^{-4}	383
1.0×10^{-4}	396
2.0×10^{-4}	494
3.0×10^{-4}	485
4.0×10^{-4}	484
5.0×10^{-4}	492

Adsorption Isotherm of Sulfate Ions on Iron in the Presence of Chloride Ions. The isotherm was repeated, except that chloride ion was added. Its concentration was 2.64 times the sulfate ion concentration at all concentrations. The data are given in Table 9 and plotted in Figure 4. The counting data are averages of the counts of four separate coupons.

In the presence of chloride, the activity picked up continues to rise even after a concentration of about 2.0×10^{-4} M is reached.

Another isotherm was run in sulfate solutions containing chloride. In this case, the concentration of chloride ion in all the solutions was the same, 1.0×10^{-3} M. The data are shown in Table 10, and plotted in Figure 5.

These data confirm those given in Table 9, showing the same increase in adsorption at the higher sulfate concentrations.

Figure 3
Adsorption of Sulfate Ion on Iron
Room Temperature, pH 7

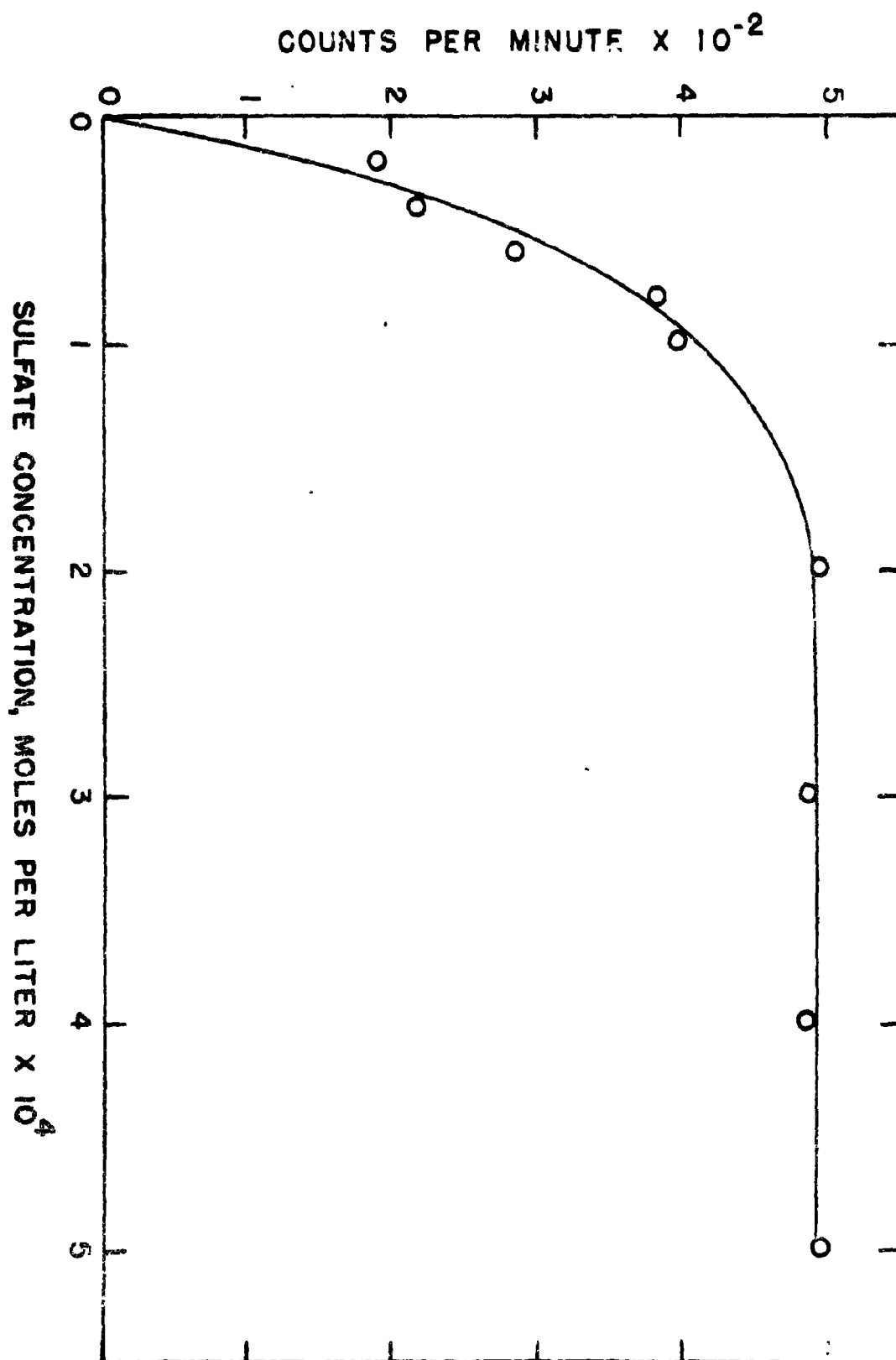


Figure 4
Adsorption of Sulfate Ion on Iron
in the Presence of Chloride Ion
Chloride Ion Concentration 2.64 times the
Sulfate Ion Concentration, Room temperature, pH 7

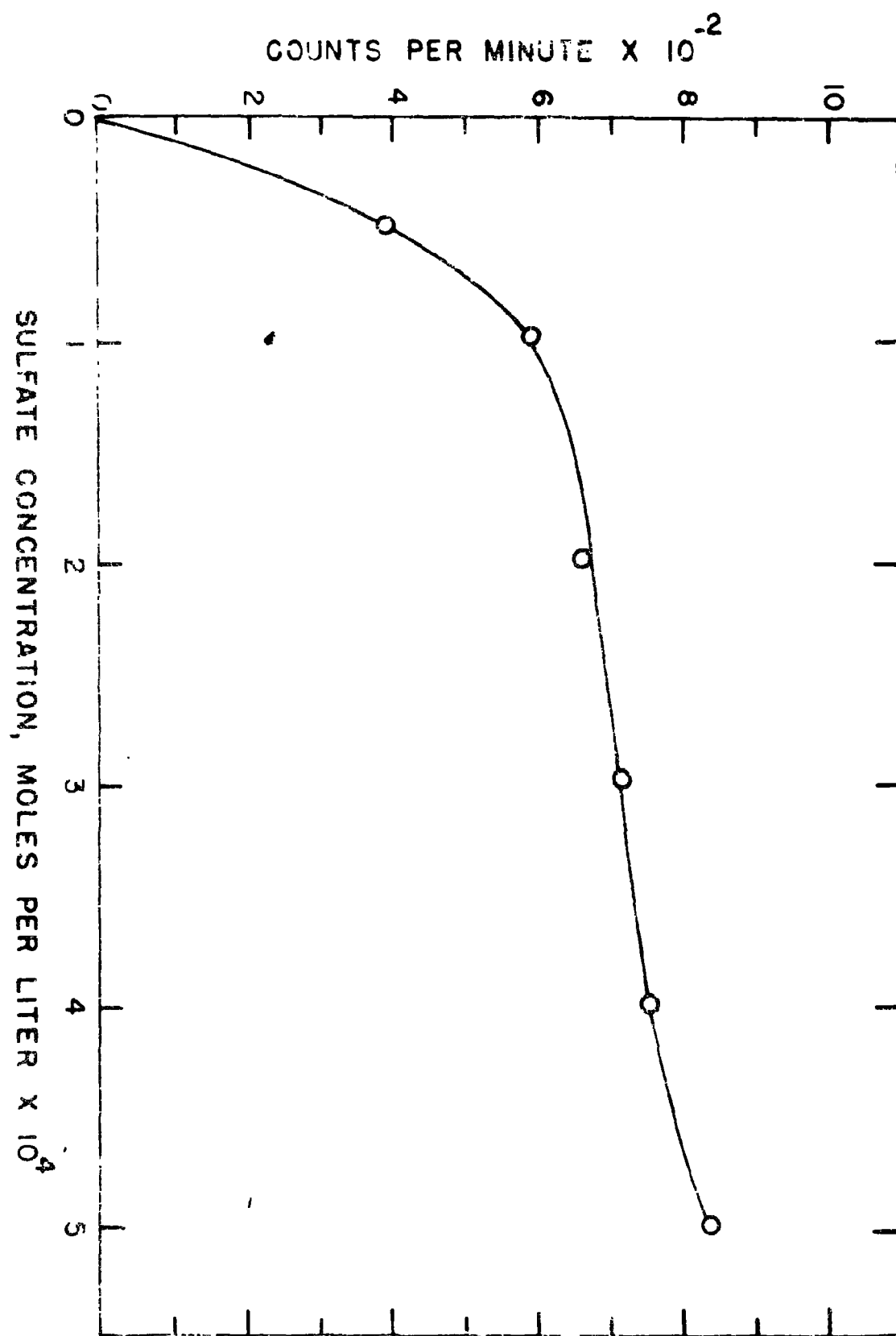


Figure 5

**Adsorption of Sulfate Ion on Iron
in the Presence of Chloride Ion
Chloride Ion Concentration 1.0×10^{-3} M
Room Temperature, pH 7**

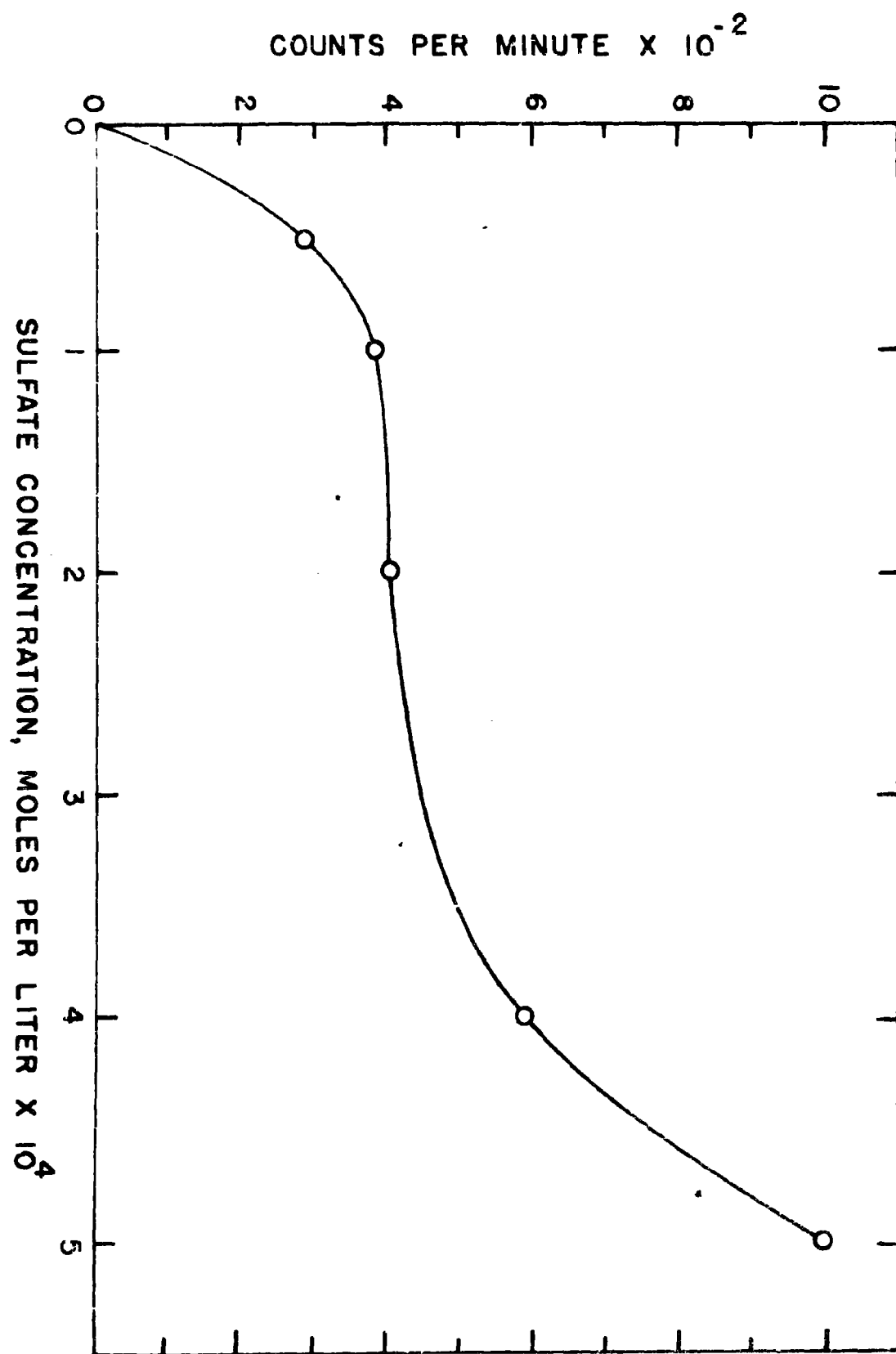


TABLE 9

Concentration <u>Na₂SO₄, Moles/l.</u>	<u>c/m</u>
0.5 x 10 ⁻⁴	394
1.0 x 10 ⁻⁴	598
2.0 x 10 ⁻⁴	664
3.0 x 10 ⁻⁴	717
4.0 x 10 ⁻⁴	752
5.0 x 10 ⁻⁴	832

Adsorption Isotherm of Sulfate on Iron in Presence of 2 x 10⁻³ M Chromate.
This isotherm was run in the same manner as the previous one, except with chromate instead of chloride. The data are shown in Table 11.

TABLE 10---

Concentration <u>Na₂SO₄, Moles/l.</u>	<u>c/m</u>
0.5 x 10 ⁻⁴	289
1.0 x 10 ⁻⁴	386
2.0 x 10 ⁻⁴	403
4.0 x 10 ⁻⁴	590
5.0 x 10 ⁻⁴	998

TABLE 11

Concentration <u>Na₂SO₄, Moles/l.</u>	<u>c/m</u>
5.0 x 10 ⁻⁵	27
1.0 x 10 ⁻⁴	59
2.0 x 10 ⁻⁴	92
3.0 x 10 ⁻⁴	83
4.0 x 10 ⁻⁴	(260)
5.0 x 10 ⁻⁴	(651)

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The last two counts are suspect because visible corrosion products undoubtedly were responsible for the high values.

Effect of pH. It was observed early in the course of the work that the pH of the solutions, which was 7 at the start of a run, decreased after a coupon had been exposed. This suggests that hydroxyl ions were removed from solution. The drop in pH amounted to one to two units, depending on various factors. A two unit drop corresponds to loss of 1.0×10^{-9} moles of hydroxyl ions from the ten ml. of solution used. This corresponds to 6×10^{14} ions.

The pH values of some of the solutions used for the isotherm shown in Table 8 are given in Table 12. This was an isotherm showing the adsorption of sulfate on iron, using sodium sulfate solutions of pH 7.

TABLE 12

<u>Concentration</u> <u>Na₂SO₄, Moles/l.</u>	<u>pH after Adsorption</u>
0.2 x 10 ⁻⁴	5.7
0.5 x 10 ⁻⁴	5.5
0.6 x 10 ⁻⁴	5.9
1.0 x 10 ⁻⁴	5.2
2.0 x 10 ⁻⁴	5.7
3.0 x 10 ⁻⁴	5.5
4.0 x 10 ⁻⁴	5.6
5.0 x 10 ⁻⁴	5.5

Similar pH values were found in runs using sulfate only.

For the isotherm whose data are given in Table 9 solutions of pH 7 were again used. Measurements of pH made after adsorption had taken place showed either no change in pH or else a slight increase, as shown in Table 13. These solutions contained chloride ions in a concentration of 2.64 times that of the sulfate ion.

For the run in which the chloride ion was kept constant at 1.0×10^{-3} M, the pH decreased after exposure of the metal to the solution. This is shown in Table 14.

When dichromate was added to the sulfate solution, there was only a slight, and probably insignificant, decrease in pH after adsorption had taken place, amounting to 0.1 to 0.2 of a pH unit.

TABLE 13

<u>Concentration</u> <u>Na₂SO₄, Moles/l.</u>	<u>pH after Adsorption</u>
0.5 x 10 ⁻⁴	7.3
1.0 x 10 ⁻⁴	7.0
2.0 x 10 ⁻⁴	7.1
4.0 x 10 ⁻⁴	7.6
5.0 x 10 ⁻⁴	7.6

TABLE 14

<u>Concentration</u> <u>Na₂SO₄, Moles/l.</u>	<u>pH after Adsorption</u>
0.5 x 10 ⁻⁴	6.0
1.0 x 10 ⁻⁴	6.3
2.0 x 10 ⁻⁴	6.7
3.0 x 10 ⁻⁴	---
4.0 x 10 ⁻⁴	7.0
5.0 x 10 ⁻⁴	6.9

An isotherm was run in sulfate solutions adjusted to pH 11. The data are shown in Table 15 and are similar to, though somewhat lower than, those for the isotherm run at pH 7; that is, there was little effect on the amount of activity picked up by the coupons, despite the relatively high hydroxyl ion concentration. The pH values after adsorption are shown in Table 15 also, and it is seen that the decrease in hydroxyl ion concentration is virtually constant, regardless of the amount of sulfate in the solution or adsorbed on the coupon.

The run was repeated in solutions in which the hydroxyl concentration was 0.1 M (measured pH 12.5) and there was virtually no activity found on the coupons.

The first run in which the pH of the solutions was varied while the sulfate ion concentration remained constant at 1.0 x 10⁻⁴ M was made in the pH range between 7 and 10, and ten ml. of each solution was used. The results showed that pick-up was constant, regardless of initial pH. The pH

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of the solutions decreased, however, during the run, and ranged from 6.4 to 7.7 after adsorption had taken place. This run was repeated using one hundred ml. of solution, and extending the pH range to 12. After the run, the pH was found to be unchanged. The data are shown in Table 16. The amount of activity on the coupons is constant through a pH range of 7 to 10, then shows an abrupt drop.

Adsorption Isotherms with Chloride and Chromate. Although isotherms were run with active chloride and chromate, no usable data were obtained.

TABLE 15

<u>Concentration</u> <u>Na₂SO₄, Moles/l.</u>	<u>c/m</u>	<u>pH after Adsorption</u>
0.2 x 10 ⁻⁴	93	8.5
0.4 x 10 ⁻⁴	125	8.5
0.6 x 10 ⁻⁴	287	8.4
0.8 x 10 ⁻⁴	305	8.4
1.0 x 10 ⁻⁴	319	8.4
1.5 x 10 ⁻⁴	286	8.5

TABLE 16

<u>pH</u>	<u>c/m</u>
7	490
8	524
9	478
10	450
11	38
12	4

Accuracy of Data

Surface Area. The variation in surface area from one coupon to another prepared in the same way is not known a priori, but it is probably significant. It was found in this laboratory (19) that surface areas of coupons polished in the same manner but by different persons differed considerably in true surface area. Although coupons used in the present work were all polished in the same manner and by the same person, they must nevertheless be expected to exhibit some differences because of variations in pressure when polishing and length of time in polishing. To obviate this to some extent the surface area measurement was made using 5 coupons. These had a total apparent area of about 28 cm².

On the basis of considerable experience in this laboratory, the surface area measurement is accurate to $\pm 10\%$. Three separate area measurements were made on these coupons. Before each run, they were polished with #2 emery and treated in the same manner as the coupons used in the adsorption runs. The roughness factors found varied from 2.9 to 3. One area measurement was made in which the coupons were polished with #4/0 emery. The roughness factor in this case was found to be 2.6.

Variation in Pick-up with Preparation of Surface. Since the coupons polished with #2 and #4/0 emery have about the same roughness factor, the wide variation in activity picked up by coupons prepared in this manner must be due to some other factor than differences in surface area. This is referred to later. The surface areas of coupons treated in other ways, e. g., by etching, were not determined, but it is unlikely that there was any great change.

Analysis for Iron. The method used is claimed to be capable of detecting iron in a concentration of one part in fifty million; however, the optimum range of concentration of colorimetric analysis is 0.5 to 6 ppm. The solutions analyzed showed between 99 and 100% transmittancy, which indicates that considerably less than 0.5 ppm. was present in the solution. This amount is equivalent to the dissolution of 1.8×10^{-7} moles of iron. No pitting or corrosion of the coupons was visible, and autoradiographs showed no localization of activity, as was always the case when corrosion occurred.

Variations in Counting Data. In counting aliquots of the active solutions to determine the number of ions present, the method first employed was to evaporate 15 microliters of the solution (pH 7) on a coupon which had been prepared in the same manner as those to be used in the adsorption runs. This sometimes gave erratic values, and it was necessary to count a number of aliquots before a satisfactory value was obtained. There was always doubt as to the accuracy and reproducibility of the results unless a large number of samples was taken. Therefore active solution was evaporated on glass cover slides, and this gave quite

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reproducible results. In a series of measurements, the individual values never differed more than 5% from the average, and the difference was usually under 2%. In making these counts, at least two samples were counted; but comparison of counts made over a long period of time showed that all were the same, within 5%, after correcting for decay.

It was necessary to introduce a correction factor, however, since counts on glass and iron were not the same. There was a constant difference, which was determined as accurately as possible by counting samples on coupons and slides, and calculating a correction factor from the averages. The count on the coupons was 1.37 times as great as that on the glass slides.

Individual coupons always showed the same count, within small differences, when counted again. Values obtained from different coupons prepared in the same manner and exposed to solutions of the same concentration were sometimes extremely close, and occasionally markedly different. Most often they varied within the limits of about $\pm 20\%$ of the average of the counts of all the coupons. For example, the counts/min. of 8 different coupons, all prepared and treated in the same manner were: 214, 205, 222, 150, 169, 187, 210, 203. The average is 195. The percent difference of each value from the average is: +10, +5, +14, -24, -13, -4, +8, +4.

In some cases, extremely high counts were obtained, but it was always found that these coupons were corroded, and the data were discarded. This happened when oxygen got to the solution.

Presence of Oxygen in Solutions. When saturated with air at 25°C , ten ml. of water contain approximately 2.6×10^{-6} moles of oxygen. A large proportion, but not all, of this oxygen is removed by bubbling nitrogen gas through the solution. Since the iron analysis showed less than 1.8×10^{-7} moles in the ten ml. of solution, and since one-half mole of oxygen is necessary to react with one mole of iron, the amount of oxygen used up during the time the coupon was in the solution was 0.9×10^{-7} moles. Actually there was much less, since 1.8×10^{-7} moles is the maximum amount of iron which could be present, and the analysis showed much less than this. Assuming that the iron dissolved as ferrous ion, it would not precipitate even at the site of dissolution because of low pH. If iron were in the solution as ferric ions, unlikely, considering the low oxygen concentration there would be 1×10^{-12} moles present in the ten ml. of solution at pH 7, as calculated from the solubility product. Thus, some ferric hydroxide might be precipitated on the coupon. However, no corrosion was visible here, and none showed on autoradiographs. If ferric hydroxide were precipitated in the solution it would have been found in the analysis, since the solutions were acidified before testing for iron.

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The oxygen concentration in the solution was therefore low all during the run, and was never enough to cause corrosion of the coupons. The oxygen concentration in the box was higher, however, and oxygen was never completely removed despite continued flushing with nitrogen.

Amount of Chloride Present in Active Sulfate. The active sulfate solution was electrolyzed to remove chloride ions. The final concentration of chloride ions was not known, but under the conditions used was less than 1×10^{-5} M. Using this value, the concentration of chloride ions in the solutions used in the adsorption runs may be calculated. In making up these solutions, 15 microliters of active solution was added to each 50 ml. of solution. The chloride concentration in these solutions would thus be 0.3×10^{-9} M. Since the sulfate ion concentration in the solutions was 5.0×10^{-4} M, the chloride ion concentration is not significant.

Depletion of Solutions. There was negligible depletion of sulfate ions even at the lowest concentrations. This was calculated from the amount of activity found on the coupons and the amount known to be in the solution originally, and corroborated by counting some of the solutions both before and after adsorption. There was no measurable loss to the walls of the test tubes.

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Discussion

The experimental evidence obtained indicates that sulfate ions are chemisorbed on iron surfaces. The potential of the local cells is not enough either to reduce the sulfate ion to sulfur or to oxidize it to persulfate. These reactions would require +0.47 and -1.5 volts, respectively, at unit activity and 25°C. There is no reaction between the metal and the solution at the pH values used, so there is no possibility of sulfate being incorporated chemically into any reaction product. The sulfate ions found on the surface must therefore be adsorbed as such.

The difficulty in removing the adsorbed ions from the surface indicates that they are chemisorbed. This is substantiated by the fact that less than a monolayer was adsorbed in all cases except for adsorption on coupons polished with fine emery, when as much as 1.75 monolayers were found. This high value is discussed later. Incidentally, the roughness factor of 3 with #2 emery indicates that all the area is on the surface; that is, there are no pores.

Effect of Oxide Layer. In all the adsorption studies made there were certain variations in the data which were accountable to such things as changes in surface area from coupon to coupon, as explained previously. Marked and consistent differences obtained under certain conditions are not of this kind, however, and other causes were sought.

This is the case when the data in Table 7 are examined. In this run coupons prepared in two different ways were used. One set of coupons was polished with #2 emery and the other with #4/0 emery. The former acquired an average of about one fifth the activity taken up by the latter. This difference cannot be attributed to difference in surface areas, since the roughness factors are 3.0 and 2.6 respectively.

The only other difference in the coupons is the amount and kind of oxide present on the surface. Coupons polished with fine emery paper almost always build up visible oxide films while with coarse grit film becomes visible only occasionally. It is likely that the coupons polished with the finer emery have more oxide on the surface than do the others, and that this greater amount of oxide is responsible for the greater pick-up of sulfate ions.

If it is assumed that sulfate is adsorbed by the oxide on the surface, then both sets of coupons should have acquired the same activity. With the less highly polished coupons, however, the oxide varies in thickness over the surface, and the sulfate may adsorb more on the thicker patches of oxide. On this basis, when the surface is highly polished, the oxide layer should be more uniform, and sulfate pick-up should be more evenly distributed. In all cases, however, there was an even distribution of activity over the surfaces of the coupons, as shown by autoradiographs. Any uneven distribution of oxide and hence of activity is therefore of microscopic dimensions.

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Another possibility is that the solution might penetrate a heavier oxide and be held in the pores or provided increased surface for adsorption in the channel walls. The fact that more than one monolayer appears to have been absorbed on the more heavily oxidized surface supports this contention.

A third possibility is that the difference in activity is not caused by the oxide on the surface, but rather by the underlying metal. The more highly polished metal would be covered by a Beilby layer but the less highly polished metal might show only some distortion. It is known (8) that there is a difference in the amount of activity picked up by distorted and undistorted surfaces but it is not believed to be the case here, however. First of all, every coupon had to be polished for so long a time in order to obtain a plane surface that each end up with the same type of surface, a Beilby layer. (The final surface was always bright and showed no visible oxide.) Second, the differences obtained by Simnad and Ruder (8) with distorted and undistorted surfaces were due to ions, e.g., Co^{++}_2 plating out on the undistorted cathodic areas. As pointed out previously, there is no chemical reaction in the case of sulfate ions.

It is believed that of these explanations, the one based on the penetrability of the oxide layer is the most probable, although the postulated change in surface area was not proved to have taken place.

Adsorption Rate and Concentration. The variation in the amount of sulfate ion adsorbed as a function of time is interesting. The apparent increase in adsorption followed by a decrease to a constant value was reproducible. In the middle portion of the curve two to three times as much sulfate is adsorbed as on coupons exposed for longer periods of time, but this sulfate is not firmly adsorbed. Sulfate adsorbed during time intervals under about fourteen hours can be removed by continued washing, except for a fraction which seems to be very firmly adsorbed. The sulfate which can be washed off is nonetheless held firmly enough so that it is not removed by the amount of washing sufficient to remove all but chemisorbed sulfate from coupons exposed to the solutions for long periods of time.

This effect is not correlated to the pH change in the solutions, since the same pH change was noted in all solutions regardless of the length of time the coupons had remained in them.

It might be that this is an orientation effect such as found by Hackerman and Glenn (20) in their studies of adsorption of polar organic molecules on steel. The central part of the curve would then show a period in which sulfate ions were adsorbed, some firmly, but others loosely and more or less piled up, preventing some adsorption sites from being used. After a while the less firmly held ions go back into solution and these sites are gradually freed. They then become available to adsorb ions directly. The filling of all the adsorption sites takes about fourteen hours.

Competitive Adsorption.

That there is competition between adsorbing ions is clearly shown by the experimental results, e.g. see Table 11 regarding chromate and sulfate. The chromate ion was shown to be firmly adsorbed on steel by (12). When present in concentrations equal to or greater than the sulfate ion concentration, it decreases sulfate adsorption greatly. Considering the similarity in the two ions, it is likely that they use the same adsorption sites. Not only can the chromate ion adsorb on the surface; there is also the possibility that it may react and be incorporated into the oxide film as the trivalent oxide. In an air-free system, however, it is believed that only adsorption takes place.

The effect of the hydroxyl ion is the same. Between pH 7 and 10 there is some adsorption of hydroxyl ions on the coupon, as indicated by the change in pH. At pH 7 this amounts to about 0.01 monolayer of hydroxyl ions, and the amount adsorbed increases rapidly with rise in pH, until the adsorption of many monolayers is indicated. Up to pH 10 the amount of sulfate adsorbed is not affected, and there is apparently no competition at this stage. At higher pH values there is competition, since the uptake of sulfate ions is definitely impeded. The uptake of hydroxyl ions is apparently not chemisorption at high pH values, since enough hydroxyl ions are removed from the solution to form many monolayers. However, it is not possible to state categorically that reaction occurs because if it did, more sulfate should be adsorbed. The hydroxyl ions first adsorbed may acquire others by hydrogen bonding to provide a true multi-layer which would not require increased sulfate adsorption.

The chloride ion has an unusual effect. At concentrations about the same as or somewhat greater than the concentration of the sulfate ion, it increases the amount of activity adsorbed on the surface. At very high concentrations it completely prevents adsorption of sulfate ions. The cause of this increase in adsorption may be attributed to changes in the surface. The efficiency of the chloride ion in breaking down passivity has been attributed to the ability of the chloride ion to penetrate the oxide film on the metal (21). If this is true, then as a result there is certainly some change in the surface, which might cause fresh adsorption sites to be available to the sulfate ion.

Other possibilities are that the chloride ion is capable of complexing with the iron in the oxide layer, or that chloride ions adsorb on the surface (22). Though the mechanism is not known, it was found that when chloride adsorbed on the surface of stainless steel, corrosion occurred more readily. The complexing or adsorption of the chloride ion may change the surface in such a way as to make more sites available for adsorption, or, if oxygen is present in the solution, for corrosion.

It is clear from this work and from that done by Powers and Hackerman (12) that the sulfate and chromate ions are chemisorbed on the surface. It is thought that the hydroxyl ion may chemisorb at low concentrations,

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forming a bond between the hydrogen of the hydroxyl ion and the oxygen of the oxide. The contact potential measurements made by Powers bear this out, showing that the oxygen atoms of the hydroxyl ion is farthest from the surface.

At higher concentrations there may be reaction with the surface; at any rate, many monolayers are adsorbed. There is the other possibility that high concentrations of hydroxyl ions peptize the surface. This does not seem likely, from the work presented here, for while a large amount of hydroxyl ions was picked up at pH 10, the amount of sulfate picked up was the same, indicating no change in surface area.

The case for the chloride ion is not clear. Other than the competition studies made, no data were obtained in the course of the present work which would throw light on the matter. The fact that it can, in sufficient concentration, prevent adsorption of sulfate, indicates that it is adsorbed. The studies made by Marshall (10) bear this out.

Nature of Surface. The fact that less than a monolayer is adsorbed from sulfate solutions indicates that the surface is not uniform, but this lack of uniformity is such that it does not show up in autoradiographs. Since autoradiographs would show differences which were microscopic, these variations in the surface must be very small, probably of atomic dimensions. From the data obtained using various types of surfaces, the amount of sulfate adsorbed is seen to be related to the previous treatment of the surface, such as abrading, etching, treating with chromate, etc., and can often be explained on this basis. The amount and distribution of oxide is an important factor in determining the amount of adsorption especially in the absence of chemical treatment of the surface.

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